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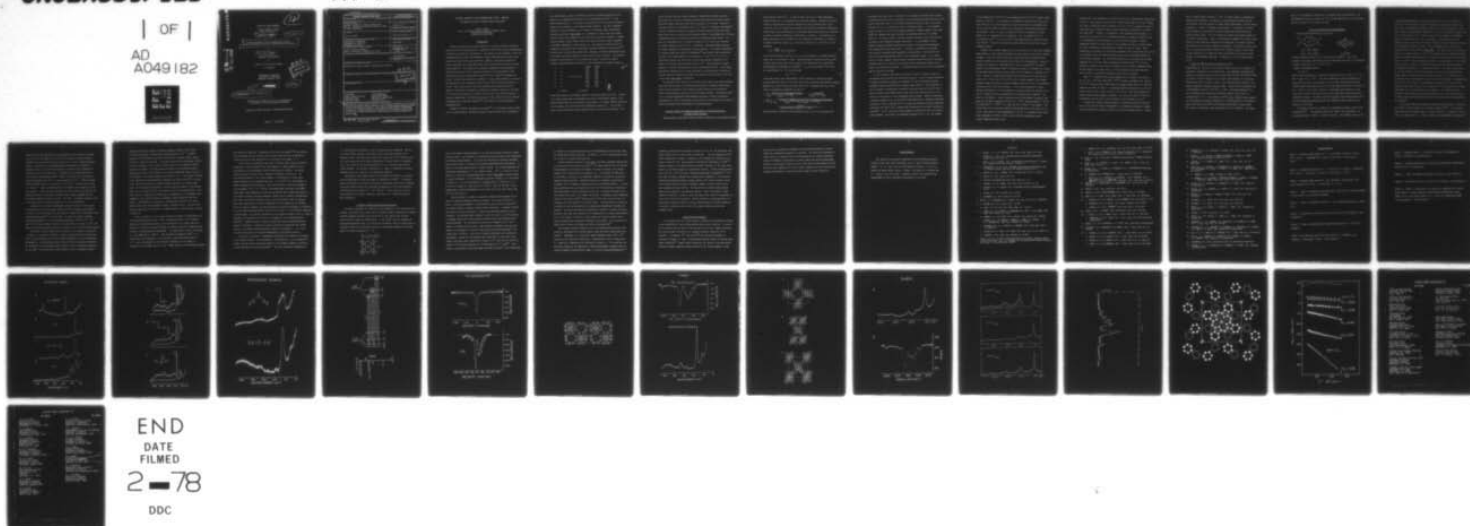
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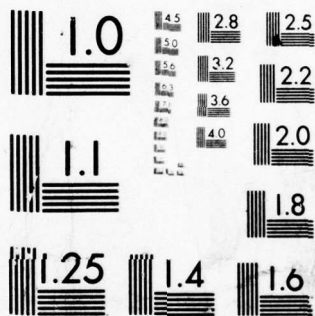
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RATIONAL SYNTHESIS OF NEW UNIDIMENSIONAL SOLIDS: CHEMICAL
AND PHYSICAL STUDIES OF MIXED VALENCE POLYIODIDES

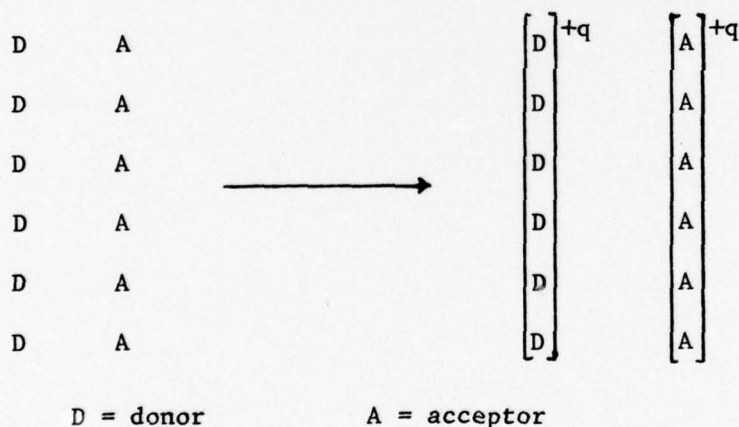
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Introduction

There has recently been intense interest on the part of chemists and physicists in the solid state properties of materials which contain strong unidimensional structural and electronic interactions.¹ The reason for this interest is that such one-dimensional and quasi one-dimensional systems sometimes exhibit rather spectacular and highly anisotropic electrical, magnetic, and optical properties.¹ Several materials [e.g., TTF-TCNQ, $(\text{SN})_x$] have stimulated much activity in solid state science.^{1,2} New organic and coordination compounds with quasi-metallic characteristics have forced a constant reevaluation and improvement of both theoretical models and experimental expectations for cooperative phenomena in solids. Clearly these studies are leading to a deeper understanding of the nature and magnitude of those fundamental factors which control electron transport in solids. This recent activity has also stimulated an exciting new field of chemical science which concentrates contemporary synthetic expertise on the goal of tailoring new molecules for specific (in this case solid state) properties: "molecule engineering." The practical outcome of these efforts may be an entirely new generation of electronic materials^{2,3} and possibly even high temperature superconductors⁴.

A number of features are generally believed^{1,2,5} to facilitate electron transport in stacked organic, inorganic, and metal-organic systems such as Krogmann's

salt $[K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O]$, TTF-TCNQ, and others (including some which do not undergo a low temperature transition to the semiconducting state⁶). In the Hubbard terminology¹, it is desirable to minimize U (the site electron correlation energy) and to maximize t (the charge transfer integral). The most reasonable approach to these requirements is to choose for stacking, highly delocalized, polarizable molecules (vide infra). It is assumed, of course, that the stacked moieties occupy crystallographic sites which are as similar as possible. Another closely related, crucial feature which only recently has been widely recognized as extremely important is mixed valency, i.e. the molecular entities which are connected in series must have fractionally occupied electronic valence shells^{1c,7}. A crucial test of solid state theory and a challenge to chemical methodology would be to devise a rational synthesis of such "mixed valence" lattices. One plausible approach we have pursued is to co-crystallize stacks of planar (to promote stacking) conjugated donor molecules, D, with an appropriate acceptor system, A,



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which would remove a non-integral amount of electronic charge per D unit. Ideally the A moiety should also be polarizable and must be sufficiently compact, to be easily incorporated into the lattice of $(D)_n$ stacks. To promote "partial oxidation" of the D units, the A must form stable polynuclear anions, A_n^{-1} . Thus in $AD_{1.0}$ each A would increase the formal oxidation state of each D by the fraction $+1/n$.

It will be seen that this simple strategy is impressively effective when the donor units are a variety of readily accessible and chemically flexible organic and metal-organic macrocycles and when the acceptor, A, is iodine. Because of the high stability of polyiodides such as I_3^{-1} and I_5^{-1} in nonpolar environments⁸ (lattices composed principally of organic functional groups) and because their shape allows them to occupy relatively narrow channels in one-dimensional lattices, polyiodide acceptors are favorably suited for introducing mixed valency. In a solid of stoichiometry DI, if iodine is present as I_3^{-1} , then D has increased its formal oxidation state by +0.33. Furthermore, iodine-containing acceptors are readily amenable to spectroscopic characterization. The powerful combination of resonance Raman⁹ and iodine -129 Mössbauer¹⁰ spectroscopy readily identifies the form of the iodine present in the lattice, i.e. I_2 , I^{-1} , I_3^{-1} , I_5^{-1} or a combination thereof, and thus allows a direct and accurate estimation of the extent of electronic charge transfer from D to A¹¹. This technique is easily applied to even non-crystalline and severely disordered materials. Such charge distribution information is of great importance in refining present theories of electron transport and has never before been acquired with such ease or for such a wide range (vide infra) of materials.

The purpose of this article is to briefly survey some of the recent research which has been conducted at Northwestern University on rationally synthesizing mixed valence materials by the strategy outlined above, and on studying the various physicochemical properties of the resulting products. The physical basis of the resonance Raman/iodine-129 Mössbauer technique of charge distribution measurement will first be discussed, then results will be reviewed in the areas of partially-oxidized metal bisdioximates and phthalocyanines.

Resonance Raman/I-129 Mössbauer Measurement of Charge Distribution
in Mixed Valence Lattices

Resonant Raman scattering⁹ provides valuable information on polyiodide molecular

and electronic structure¹². As will be seen, each type of iodine-containing species gives rise to a characteristic scattering spectrum. Moreover, the intensities of iodine-centered spectral features are vastly enhanced when a laser excitation source is brought into resonance with molecular electronic transitions. Unlike simple infrared absorption, the resonance Raman scattering is not obscured by other, frequently extraneous, normal modes of vibration. The intensity of a Raman transition, $I(\nu_r)$, averaged over all molecular orientations, is related to the Raman scattering tensor, $R_{\rho\sigma}$, as given in equation (1). Here $I(\nu_0)$ is the intensity

$$I(\nu_r) = \frac{2^7 \pi^5}{3^2 c^4} \nu_r^4 I(\nu_0) \sum_{\rho\sigma} |R_{\rho\sigma}|^2 \quad (1)$$

of the exciting laser source (at ν_0), ν_r is the frequency of the Raman scattered light, and c is the speed of light. Quantum mechanical descriptions of $R_{\rho\sigma}$ have recently been derived which take account of both Herzberg-Teller coupling and Born-Oppenheimer nonadiabatic coupling^{9,13}. $R_{\rho\sigma}$ can be expressed as the sum of two contributions (eq. (2)) which describe

$$R_{\rho\sigma} = A + B \quad (2)$$

scattering arising from Franck-Condon allowed transitions involving a single excited electronic state (A) and those which derive intensity via vibronic coupling between two or more excited electronic states (B). Expression for the A and B terms are presented in equations (3) and (4).

$$A = \frac{1}{h} \sum_{e,v} \left[\frac{(g^0 | \mu_\rho | e^0)(e^0 | \mu_\sigma | g^0) \langle g | e v \rangle \langle e v | g | \rangle}{\nu_{ev,gi} - \nu_0 + i\Gamma_{ev}} + \frac{[\rho \leftrightarrow \sigma]}{\nu_{ev,gj} + \nu_0 + i\Gamma_{ev}} \right] \quad (3)$$

$$B = \frac{-1}{h^2} \sum_{e,v} \sum_{s,u} \left[\frac{(g^0 | \mu_\rho | s^0)(s^0 | (\partial H / \partial Q)_\rho | e^0)(e^0 | \mu_\sigma | g^0) \langle g | s u \rangle \langle s u | e v \rangle \langle e v | g | \rangle}{\nu_{su,gi} - \nu_0 + i\Gamma_{su} (\nu_{ev,gi} - \nu_0 + i\Gamma_{ev})} + \frac{[\rho \leftrightarrow \sigma]}{(\nu_{su,gj} + \nu_0 + i\Gamma_{su})(\nu_{ev,gj} + \nu_0 + i\Gamma_{ev})} \right]$$

These describe a transition from vibrational state i to j in the ground state

electronic level (g_i to g_j). Here $|e^0\rangle$ is the adiabatic electronic wave function of excited electronic state e , evaluated at the equilibrium nuclear positions of the ground electronic state, μ is the dipole transition operator, $|ev\rangle$ is the wave function for the v th vibrational level of electronic state e . In the denominators the terms ν_{ev, g_i} are the frequency separation between vibronic levels, and the Γ_{ev} are damping terms which describe the radiative widths of the vibronic states ev . The term s refers to another excited electronic state (other than e), the prime on the summation excludes terms where $s = e$, and $(\partial H / \partial Q)_0$ is the vibronic coupling operator describing the change in the electronic Hamiltonian with displacement along normal mode Q . $(\partial H / \partial Q)_0$ is evaluated at the ground state nuclear coordinates and transforms as normal mode Q . The second term in each of the above expressions refers to the non-resonant regime. For A terms, only the totally symmetric normal modes of molecular vibration should be resonant enhanced, while for B terms only those modes which vibronically couple s and e states will exhibit this behavior. In principle these effects can be distinguished via the excitation profiles.

As can be readily appreciated, equations (3) and (4) contain a wealth of information about molecular and electronic structure. For the present discussion of charge distribution analysis, the emphasis will be on deriving structural information about polyiodides from resonance Raman studies. Since equations (3) and (4) provide no information on empirical quantities such as force and interaction constants (and indeed whether useful structural deductions will be possible) it is necessary to first investigate model systems. Figure 1A illustrates a solution spectrum of I_2 , and 1B a solid state spectrum of a material containing isolated I_3^{-1} units $[(C_6H_5)_4As^+ I_3^-]^{14}$; besides the extremely intense fundamental vibrations (205 and 114 cm^{-1} , respectively) characteristic overtone scattering is observed.¹⁵ In I_3^{-1} , only the totally symmetric vibration is seen to be appreciably enhanced. The actual I-I stretching frequency in I_3^{-1} , i.e. the average

of the symmetrically (110 cm^{-1}) and antisymmetrically (145 cm^{-1})⁸ coupled normal modes, is 128 cm^{-1} . This represents a considerable lowering of the force constant from that in I_2 and illustrates an important feature of polyiodide electronic structure which is evident in the vibrational spectroscopy and also in the metrical data: I_2 acts as a Lewis acid and the coordination to Lewis bases, e.g. I^{-1} decreases the I-I bond order. The I-I distance in I_2 is 2.72 \AA , while in I_3^{-1} it is ca. 2.92 \AA .⁸ Approximate molecular orbital calculations¹⁶ on I_3^{-1} show that the highest occupied molecular orbital has I-I antibonding character.

Turning now to further examples in the solid state, it is seen that resonance Raman spectra of more complex polyiodides of known structure can also be readily assigned. In no case to date does factor group splitting (correlation field effects) introduce a serious problem in the spectral interpretation. Figure 1C presents the spectrum of $(\text{C}_6\text{H}_5\text{CONH}_2)_2\text{H}^+\text{I}_3^-$, which structurally¹⁷ is known to consist of one-dimensional chains of symmetrical (equal I-I distances) I_3^- units. The resonance Raman spectrum clearly shows that the compound is composed of I_3^{-1} units. Because of strong lattice forces, the triiodide units in CsI_3 are distorted ($\text{I-I} = 2.83(2)$ and $3.03(2)\text{ \AA}$)¹⁴; this is readily apparent in the Raman spectrum (Figure 1D) where the lowered symmetry gives rise to two $\nu\text{I-I}$ emissions (further split by solid state effects). For the characterization of mixed valence polyiodides it is also reasonable to inquire whether the presence of I_2 and I_3^{-1} together could be recognized by the resonance Raman technique. The answer is affirmative. Figure 2 presents spectra and schematic structural diagrams for the model compounds $(\text{Cs}^+)_2(\text{I}_3^{-1})_2 \cdot \text{I}_2$ ^{18a}, $(\text{phenacetin})_2\text{H}^+\text{I}_3^{-1} \cdot \text{I}_2$ ^{18b}, and $(\text{C}_2\text{H}_5)_4\text{N}^+\text{I}_3^{-1} \cdot 2\text{I}_2$ ^{18c}; it is clear the both I_2 and I_3^{-1} are present. The dotted lines in the structures indicate weak interactions on the order of $3.42\text{--}3.55\text{ \AA}$. These cause a slight lengthening of the " I_2 " I-I distances in the above three compounds to $2.83(2)$, $2.748(2)$, and $2.735(3)\text{ \AA}$, respectively, and a roughly commensurate drop in the

observed " I_2 " ν I-I frequencies to 171, 187, and 183 cm^{-1} , respectively. Distortions in the I_3^{-1} units appear to give rise to a second band in the ca. 150 cm^{-1} region. This band is relatively weak in relation to the ca. 110 cm^{-1} transition except in Cs_2I_8 where the triiodide is rather severely distorted (triiodide I-I = 2.84(2) and 3.00(2) Å)^{18a}. Though it is premature to draw quantitative conclusions, it can also be seen that the ν I-I scattering increases in intensity relative to the I_3^{-1} scattering as the proportion of I_2 in the lattice increases. Another significant feature of these spectra is the presence not only of overtone bands, but also of combination bands between the various I_2 and I_3^{-1} modes. These transitions are assurance of the physical proximity of the oscillators and rule out the possibility that the observed spectrum arises from a mechanical mixture of two different compounds. The electronic transitions in the solid state of these compounds as well as most other polyiodides are rather broad.^{12,19} For the complexes of Figure 2, the relative intensities of the various fundamental transitions change by no greater than ca. $\pm 10\%$ on varying the exciting line from 4880 to 6471 Å. More detailed excitation studies are in progress.

When I^{-1} is symmetrically disposed between two I_2 moieties, the result is the I_5^{-1} ion. Both bent $((\text{CH}_3)_4\text{N}^{+1} I_5^{-1})^{20a}$ and linear $[(\text{trimesic acid} \cdot \text{H}_2\text{O})_{10} \cdot \text{H}^{+1} I_5^{-1}]^{20b}$ forms have been identified; the resonance Raman spectra of these two compounds are shown in Figure 3. Stretching vibrations centered at ca. 160 cm^{-1} reflect the fact that, unlike in I_3^{-1} , the I^{-1} in I_5^{-1} must now distribute its electron density between two I_2 acceptors. The first-order result is that the perturbation from the free I_2 force constant is not as drastic as in I_3^{-1} .

Although the resonance Raman technique is obviously a powerful structural tool, at its present stage of development it is limited with respect to quantitatively analyzing the relative amounts of various polyiodide species. Further-

more, it cannot detect isolated I^{-1} ions. For these reasons a complementary spectroscopic technique, also immune to crystallographic disorder and non-crystallinity, has been applied to charge density measurements in mixed valence polyiodides: iodine -129 Mössbauer spectroscopy. This method of recoilless nuclear gamma ray spectroscopy¹⁰ involves transitions between ground and excited nuclear states. For I-129 these have nuclear spin quantum numbers of 5/2 and 7/2 respectively. Figure 4 illustrates the maximum of 8 allowed transitions for this particular nucleus and the appearance of a typical spectrum when iodine is in an axially symmetric environment. The chemical isomer shift (δ) is a hyperfine term which reflects the s electron density at the iodine nucleus (relative to the gamma ray source) and affects the overall velocity position of the Mössbauer spectrum. In equation 4, Z is the atomic number, ϵ_0 the

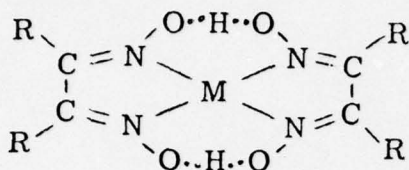
$$\delta = \frac{1}{5\epsilon_0} Ze^2R^2 \frac{\delta R}{R} (|\Psi_s(0)_{\text{absorber}}|^2 - |\Psi_s(0)_{\text{source}}|^2) \quad (4)$$

permittivity of a vacuum, R is the nuclear radius, and δR is the change in R on making a transition to the excited state. The quadrupole splitting (QS) reflects the energy differences which arise between nuclear spin angular momentum states when the symmetry of the electric field gradient at the nucleus descends from cubic to axial or lower. This splitting can be related to the nuclear quadrupole coupling constant, e^2qQ/h . Figure 5A(top) illustrates the I-129 Mössbauer spectrum of TTF $^{129}I_{0.71}$ (TTF = tetrathiofulvalene);²¹ the lack of quadrupole splitting and the derived chemical isomer shift are characteristic of I^{-1} . The spectrum of $Cs^{129}I_3$ (Fig.5 bottom) is more complex, but using computer simulation techniques it is easily analyzed. The analysis agrees well with X-ray data¹⁴ which indicate three kinds of iodine atoms and a long I-I bond which lends appreciable $I-I \cdots I^{-1}$ character. The advan-

tages of I-129 Mössbauer spectroscopy are apparent from this discussion. The disadvantages include the expense of ^{129}I , the high radioactivity of the sources, and the relatively low recoilless fractions.

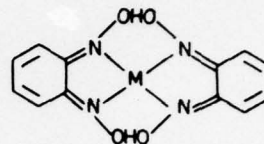
Partially Oxidized Metal Bis(dioximates)

Bis(dimethylglyoximate)Ni(II), A, was the



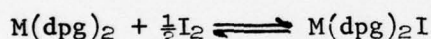
A, $\text{R} = \text{CH}_3$: $\text{M}(\text{dmg})_2$

B, $\text{R} = \text{C}_6\text{H}_5$: $\text{M}(\text{dpg})_2$



C $\text{M}(\text{bqd})_2$

earliest recognized example of a stacked d^8 metal complex²². Early work revealed that $\text{Ni}(\text{dpg})_2$ and $\text{Pd}(\text{dpg})_2$ could be reversibly iodinated (or brominated) as shown in equation (5).²³ The form of the



$\text{M} = \text{Ni}, \text{Pd}$

iodine in these complexes was variously formulated as I_2 (i.e. Ni^{+2}), I_3^{-1} (i.e. $\text{Ni}^{+2.33}$), and I^{-1} (i.e. Ni^{+3}). Since the golden-olive colored halogenated products were reported to be diamagnetic and to be more electrically conductive (pressed pellet measurements) than the starting $\text{M}(\text{dpg})_2$ materials by a factor of $10^3 - 10^4$,²⁴ it was of great interest to investigate these complexes in more detail as the first prototypes of mixed valence materials synthesized via the polyiodide strategy. The reports by Keller et. al.²⁵, which demonstrated that Ni and Pd bis(benzoquinonedioximates), C, were chemically similar added further impetus to the efforts.

The crystal structure of $\text{Ni}(\text{dpg})_2\text{I}$ was determined by single crystal X-ray diffraction^{26,27}. The palladium analogue was found to be isomorphous. The tetragonal (P4/ncc) lattice is shown in Figure 6. The $\text{Ni}(\text{dpg})_2$ units are all

crystallographically identical and stack, staggered by 90° , at intervals of $3.271(1)\text{\AA}$. This metal-metal distance represents an appreciable decrease from that found in unhalogenated Ni(dpg)_2 , 3.547\AA , but is still comparable to the Ni-Ni distance in unhalogenated Ni(dmgl)_2^{22} , 3.25\AA , and considerably greater than that in nickel metal, 2.49\AA . Metrical aspects of the $\text{Ni(dpg)}_2\text{I}$ coordination sphere are rather similar to those of Ni(dmgl)_2 . The iodine atoms in the $\text{Ni(dpg)}_2\text{I}$ structure are found in channels extending along the stacking direction and surrounded by aromatic residues. This arrangement will be seen to be a common pattern for such lattices (vide infra). The iodine atoms in the channels appear to be equally spaced at $3.271(1)\text{\AA}$ and judging from the anomalously large apparent root-mean-square amplitudes of vibration in the c direction ($0.756(11)\text{\AA}$ versus $0.234(4)\text{\AA}$ in the perpendicular direction) are disordered, i.e. the iodine atoms can occupy a number of coordinates along c and the occupancy pattern is not adequately described by the present space group. The large rms amplitudes do not then represent actual thermal motion, but rather the superposition of iodine atoms in slightly different positions along c . This could be due to a periodicity in the one-dimensional iodine chain structure which is incommensurate with the unit cell length (a one-dimensional superstructure²⁸) and in which different chains may or may not be in registry, or it may simply reflect random positioning of the iodine moieties in the channel. In optimum cases it is possible to make additional structural inferences (or to test certain models) if diffuse X-ray scattering reflections can be located between the Bragg lines, and analyzed²⁸.

The resonance Raman/I-129 Mössbauer technique was next applied to deducing the form(s) of iodine present in the $\text{M(dpg)}_2\text{I}$ materials^{26,27}. The resonance Raman spectrum of $\text{Ni(dpg)}_2\text{I}$ (Figure 7) clearly rules out the presence of either free I_2 or symmetrical I_3^{-1} . Though a highly and unprecedentedly distorted I_3^{-1}

moiety was at first considered as an explanation for the intense I-I stretch at 160 cm^{-1} and the weaker one at 107 cm^{-1} , the reason for such an unusual distortion in this particular lattice is not at all clear, or physically reasonable. Furthermore, the agreement between the spectra of the model I_5^{-1} compounds (Figure 3) and that of $\text{Ni}(\text{dpg})_2\text{I}$ is extremely close, arguing persuasively for the I_5^{-1} formulation. In addition to the Raman results, the fully refined I-129 Mössbauer data²⁷ (Figure 7) indicate site populations in excellent agreement with the 1:2:2 ratios expected for I_5^{-1} . Based on conservative estimates, there is less than ca. 3-5% I_2 or I^{-1} present and less than ca. 5-10% I_3^{-1} . Raman and Mössbauer data for $\text{Pd}(\text{dpg})_2\text{I}$ are identical to those for $\text{Ni}(\text{dpg})_2\text{I}$. Thus, this work represents the first conclusive proof that the $\text{M}(\text{dpg})_2\text{I}$ materials are partially oxidized, mixed valence compounds and that the iodine oxidation strategy is viable. The formal fractional oxidation state of the metal units has thus increased by ca. +0.20 upon iodination.

In addition to the Raman and Mössbauer spectral results, it has recently been possible to grow large enough single crystals of $\text{Ni}(\text{dpg})_2\text{I}$ and $\text{Pd}(\text{dpg})_2\text{I}$ to allow, for the first time, both four-probe dc conductivity²⁹ and diffuse X-ray scattering measurements³⁰ to be performed. We find the partially oxidized bisdiphenylglyoximates to be narrow-gap semiconductors ($\sigma_{298^\circ\text{K}} \approx 10^{-3} - 10^{-2}\text{ ohm}^{-1}\text{ cm}^{-1}$); iodine oxidation enhances the conductivity by a factor of 10^9 ! The diffuse X-ray scattering data have been collected and are presently being analyzed.

The $\text{M}(\text{dpg})_2\text{I}$ results signalled the potential of the synthetic and spectral techniques. It was next of interest to explore systems where the stacked units were in close proximity and were more highly conjugated, as in the benzoquinone-dioximates, C. The pioneering studies of Keller and his co-workers established the existence of quasi-one-dimensional materials of the stoichiometry $\text{M}(\text{bqd})\text{I}_{0.5}$, $\text{M} = \text{Ni}, \text{Pd}$;²⁵ they reported the nickel complex to have a tetragonal (P4/mcc)

crystal structure with stacks of partially staggered $\text{Ni}(\text{bqd})_2$ units ($\text{Ni-Ni} = 3.153(3)\text{\AA}$) and chains of iodine atoms running parallel to \underline{c} .³¹ An ORTEP drawing of this structure, calculated from the data of Endres, Keller, Moroni, and Weiss is shown in Figure 8A. This basic structure is interestingly related to that of $\text{Ni}(\text{dpg})_2\text{I}$ by the filling of only one-half of the available lattice channels with iodine. The iodine atoms were found to be disordered along the stacking axis and the exact identity of the iodine-containing species could not be determined. The authors proposed the presence of I_3^{-1} . The crystal structure of the iodine-free starting material, $(\text{bqd})_2\text{Ni}$, was found by Weiss³² to be monoclinic ($\text{P}2_1/\text{n}$), with stacks of canted, $\text{Ni}(\text{bqd})_2$ moieties in a "herring bone" array. The nickel-nickel distance is $3.856(2)\text{\AA}$ and the normals to the $\text{Ni}(\text{bqd})_2$ planes are at an angle of 61.8° with respect to the Ni-Ni chain direction. From these results it appeared that iodination is accompanied by a considerable rearrangement of the crystal structure, including a large increase in the Ni-Ni overlap. Surprisingly, the structure of $(\text{bqd})_2\text{Pd}$ was reported³³ to be orthorhombic (Ibam) with stacked $\text{Pd}(\text{bqd})_2$ planes extending along \underline{c} . The Pd-Pd distance was reported to be $3.202(1)\text{\AA}$. An ORTEP drawing of this structure is shown in Figure 8B.

It was of interest to us to explore several new avenues of investigation in the benzoquinonedioxime systems. These included application of the resonance Raman/iodine-129 Mössbauer method to the elucidation of the iodine identity in $\text{M}(\text{bqd})_2\text{I}_{0.5}$, further structural definition of changes induced by iodination, and extension of physicochemical measurements. The spectroscopic results on $\text{Ni}(\text{bqd})_2\text{I}_{0.5}$ are summarized in Figure 9. From the Raman and Mössbauer data¹¹ it is evident that the predominant, if not exclusive, iodine-containing species is I_3^{-1} . Thus, this material is also partially oxidized, with the degree of oxidation of the $\text{Ni}(\text{bqd})_2$ unit ca. + 0.17. Raman spectra of the palladium analogue

are essentially identical. Independent of this work an analysis^{28b} of the diffuse X-ray scattering pattern arising from the iodine chain structure in $\text{Ni}(\text{bqd})_2\text{I}_{0.5}$ reached exactly the same conclusion as to the form of the iodine: I_3^{-1} .

In the course of studying the reactions of $\text{Ni}(\text{bqd})_2$ under various iodination conditions, it was discovered³⁴ that small amounts of iodine promoted the crystallization of an orthorhombic ($P4/mcc$) modification of $\text{Ni}(\text{bqd})_2$. The extraordinary crystal structure of this compound is presented in Figure 8C. The most striking feature of the lattice geometry is the presence of large, empty channels parallel to the stacking direction. It is found³⁴ that this $\text{Ni}(\text{bqd})_2$ is nearly isomorphous with $\text{Ni}(\text{bqd})_2\text{I}_{0.5}$ since the distortion of unit cell parameters from tetragonal ($a = b = 15.553(4)\text{\AA}$) to orthorhombic ($a=16.438(4)$, $b=14.759(3)\text{\AA}$) is rather small. Thus comparison of these two structures, which differ principally in the channel occupancy, provides meaningful insight into the spatial reorganization that occurs upon partial oxidation. What is most surprising is that the changes which take place need be so small in magnitude for this system when the $\text{Ni}(\text{bqd})_2$ units are properly oriented. The major alteration in going from $\text{Ni}(\text{bqd})_2$ to $\text{Ni}(\text{bqd})\text{I}_{0.5}$ is in the stacking distance, which contracts from $3.180(1)$ to $3.153(3)\text{\AA}$ upon oxidation-- a 0.027\AA change. The relative orientation of the adjacent $\text{Ni}(\text{bqd})_2$ units in a stack is apparently not dictated in this case by the symmetries of the ligand molecular orbitals³⁵. Optimum overlap of highest occupied and lowest unoccupied molecular orbitals in $\text{Ni}(\text{bqd})_2$ is expected to require a different orientation than optimum overlap of the highest occupied molecular orbitals in $\text{Ni}(\text{bqd})_2\text{I}_{0.5}$. It is seen that these factors are not structure-determining in the present situation.

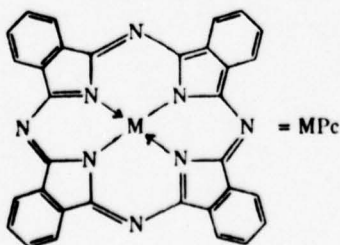
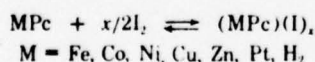
It was also of interest to investigate structurally the response to iodination of the $\text{Pd}(\text{bqd})_2$ system. We find $\text{Pd}(\text{bqd})_2\text{I}_{0.5}$ and $\text{Ni}(\text{bqd})_2\text{I}_{0.5}$ to be isomorphous³⁶. Indeed, even the diffuse scattering pattern of the palladium compound is identical to that reported for the nickel analogue²⁸. The Pd-Pd separation in $\text{Pd}(\text{bqd})_2\text{I}_{0.5}$

is $3.184(1)\text{\AA}$, which represents a 0.019\AA contraction upon iodination. This is, as in the $\text{Ni}(\text{bqd})_2$ lattice, a relatively small contraction compared to the $\text{M}(\text{dpg})_2\text{I}$ system. The other major change which takes place in the $\text{Pd}(\text{bqd})_2$ structure upon iodination can be readily appreciated in Figure 8 and is a spreading out of the lattice in the plane perpendicular to \underline{c} , to provide space for the iodine channels. The relative orientation, i.e. angle of staggering of adjacent $\text{Pd}(\text{bqd})_2$ groups in a stack does not change upon oxidation.

Sufficiently large single crystals of the $\text{M}(\text{bqd})_2$ and $\text{M}(\text{bqd})_2\text{I}_{0.5}$ materials have now been grown to allow four-probe dc conductivity studies²⁹. An approximately 10^9 increase in electrical conductivity takes place upon partial oxidation. The mixed valence crystals are narrow-gap semiconductors, with room temperature conductivities in the range $10^{-3} - 10^{-2}\text{ ohm}^{-1}\text{cm}^{-1}$. These values are close to those found for the $\text{M}(\text{dpg})_2\text{I}$ compounds, which have a ca. 0.10\AA greater metal-metal separation.

Partially Oxidized Phthalocyanine Materials

The highly conjugated (in comparison to the dioximates) flat structures, the presence of multiple redox states, and the inherent chemical flexibility of phthalocyanines suggested attractive donor molecules for the construction of mixed valence lattices using the iodine method. It was found³⁷ that the oxidation of metallophthalocyanines (MPc) or the metal-free macrocycle (PcH_2) by iodine vapor or solutions results in an extensive new class of very highly conductive "molecular metals" as shown in equation (6). The



(6)

exact stoichiometry obtained depends on the reaction procedure and can be systematically varied. The iodination is reversible and heating under vacuum regenerates the starting phthalocyanines. That these new materials are partially oxidized, mixed valence solids is supported by resonance Raman/iodine-129 spectroscopy. In Figure 10 are shown Raman spectra of typical samples. The strong fundamental and vibrational progression of I_3^{-1} are readily evident. For $x \lesssim 3$ there is no evidence of I_2 , which the aforementioned model studies (vide supra) indicate should be readily detectable. The I-129 Mössbauer spectrum of $NiPcI_{2.16}$ is illustrated in Figure 11. It is also indicative of a symmetrical I_3^{-1} molecule, i.e. $q = 1.34$ and 0.27 mm/sec vs. $ZnTe$, and the ^{129}I $e^2qQ = -1667$ and -862 MHz. Any I_2 present must, by these measurements, be less than 10% of the total iodine, and any I^{-1} is less than 5%.

Single crystals of a number of partially oxidized phthalocyanines can be grown by temperature-gradient diffusion methods. The crystal structure of $NiPcI_{1.0}$ has been determined by X-ray diffraction and is shown in Figure 12³⁸. The overall packing is typical of these kinds of materials: tetragonal ($P4/mcc$) with stacks of donors and chains of iodine atoms extending parallel to the c direction. The stacking repeat distance for the $NiPc$ units is $3.244(3)$ Å, which is somewhat longer than in the partially oxidized nickel and palladium benzoquinonedioximates. The individual $NiPc$ groups are staggered by 39.5° with respect to adjacent units in stack. Bond distances and angles within the $NiPc$ molecule are comparable to those of other planar metal phthalocyanines.³⁹ The iodine atoms of $NiPcI_{1.0}$ give rise to diffuse scattering in the diffraction photographs. Analysis of the positions and intensities of these extra lines yields a structural model consisting of chains of I_3^{-1} units with I-I bond distances of $3.00(2)$ Å and spacings of $3.72(2)$ Å between the I_3^{-1} units³⁸. This result is in excellent accord with known polyiodide structures. More importantly,

it reinforces the conclusions drawn from the Raman/Mössbauer studies that these are indeed mixed valence materials. For $\text{NiPcI}_{1.0}$, the $\text{D} \rightarrow \text{A}$ charge density transfer is thus 0.33 electron per NiPc unit.

Powder diffraction studies of other MPcI_x and PcH_2I_x compounds indicate that all have very similar crystal structures^{37,38}. It seems plausible that the various stoichiometries are related by the degree of iodine occupation of the various channels in the lattice which run parallel to \underline{c} . By eclipsing the PcNi units in the $\text{PcNiI}_{1.0}$ structure, four additional channels are created at $1/2, 0, z$ and symmetry-related positions. Complete filling of all channels would produce a tetragonal cell of comparable dimensions and the stoichiometry $\text{NiPcI}_{3.0}$. At this time insufficient data are available on any of the new materials to rigorously determine whether x varies continuously from 0 to 3 or whether mixtures of discrete phases with fixed x or x ranges are present. Preliminary iron-57 Mössbauer studies on the FePcI_x series⁴⁰ indicate that in this case x does not vary continuously, but that several FePcI_x species exist. The distribution of phases is a function of the stoichiometry and the preparative methodology (including the solvent). XPS (X-ray photoelectron spectroscopy) studies⁴¹ of NiPcI_x and PtPcI_x materials ($x \leq 3$) have been conducted at low temperature with careful monitoring of the $\text{I } 3d \ 5/2$ signal (to insure no I_2 was being lost from the surface) and in several instances with ion-sputter cleaning of the surface. In all cases only a single kind of nickel or platinum ion could be distinguished.⁴¹

The electron transport properties of the new phthalocyanine materials were initially investigated with pressed pellets using four-probe conductivity techniques³⁷. Remarkably, it is found that iodine oxidation causes a $10^9 - 10^{10}$ increase in the electrical conductivity. Representative plots of conductivity as a function of temperature are illustrated in Figure 13. It is seen that the best MPcI_x conductors are comparable to (quinolinium)(TCNQ)₂ pressed pellets in electron transport characteristics (TCNQ = 7,7,8,8-tetracyanoquinodimethane).³⁷

Generally, pressed pellet specimens are found to be ca. 10^2 less conductive than single crystal values in these types of materials. The room temperature electrical conductivity of $\text{NiPcI}_{1.0}$ crystals, in the stacking (c) direction, is in excess of $200 \text{ ohm}^{-1} \text{ cm}^{-1}$ and increases on lowering the temperature to 100°K .⁴² Further evidence for the quasi-metallic electronic structure of the PcNiI_x derivatives is provided by magnetic susceptibility studies. Faraday balance measurements from $100 - 298^\circ\text{K}$ show weak, temperature-independent paramagnetism.³⁷ The fact that the PcH_2I_x compounds have conductivities comparable to the partially oxidized metallophthalocyanines strongly implies that electron transport takes place largely through the highly conjugated ligand π electron clouds, rather than through metal-metal overlap. The new partially oxidized phthalocyanine materials are unique for two important reasons. First, they possess a great chemical flexibility in terms of metal and ligand which offers the opportunity to "fine tune" solid state properties. Second, unlike the starting materials for other highly conductive molecular solids, phthalocyanines are today produced on a millions of pounds per year scale by the pigment industry and are thus extremely cheap.

Conclusions and Prospects

It is apparent that the iodine oxidation procedure has considerable efficacy in the construction of quasi one-dimensional mixed valence lattices. It should also be obvious that the scope of this procedure, as of most chemical syntheses, has certain bounds, dictated by the intrinsic molecular properties of the reactants. For example, we²⁷ (and others^{23a}) have found that $\text{Pt}(\text{dpg})_2$ is oxidized to $\text{Pt}(\text{dpg})_2\text{I}_2$; also, perchlorophthalocyanines cannot be oxidized under normal conditions³⁸. Despite these limitations, the variety of new and unusual partially oxidized compounds already produced by this method suggests a broad

scope and that considerable refinement in the design and synthesis of highly conductive unidimensional materials is possible. The other major advantage of using iodine as an acceptor lies in the applicability of resonance Raman and iodine -129 Mössbauer spectroscopy to lattice charge distribution measurement. Hopefully the coupling of these as well as other physical measurements with the new solid state chemistry will lead to deeper insights into those factors which stabilize quasi-metallic crystals and which promote electron conduction.

Acknowledgments

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Figure Captions

Figure 1. Resonance Raman spectra of: A. I_2 in benzene solution, B. $(C_6H_5)_4As^+I_3^-$ solid, C. $(C_6H_5CONH_2)_2H^+I_3^-$ solid, D. CsI_3 solid. In all cases $\nu_0 = 5145 \text{ \AA}$.

Figure 2. Resonance Raman spectra of: A. $(Cs^+)_2(I_3^-)_2 \cdot I_2$ solid, B. $(phenacetin)_2H^+I_3^-$ solid, C. $(C_2H_5)_4N^+I_3^- \cdot 3I_2$ solid. In all cases $\nu_0 = 5145 \text{ \AA}$.

Figure 3. Resonance Raman spectra of: Top. $(CH_3)_4N^+I_5^-$ solid, Bottom. $(tri-mesic \text{ acid} \cdot H_2O)_{10}H^+I_5^-$ solid. In both cases $\nu_0 = 5.45 \text{ \AA}$.

Figure 4. Iodine -129 Mössbauer transitions and a stick plot of a typical spectrum for the nucleus in a non-cubic environment.

Figure 5. Iodine -129 Mössbauer spectra of: Top. tetrathiofulvalene $\cdot I_{0.7}$, Bottom. CsI_3 .

Figure 6. Stereoscopic view down the c axis of the unit cell of $Ni(dpg)_2I$, from reference 26.

Figure 7. Iodine -129 Mössbauer and resonance Raman spectra ($\nu_0 = 5145 \text{ \AA}$) of $Ni(dpg)_2I$.

Figure 8. View down the c axis of the unit cells of: A. $Ni(bqd)_2I_{0.5}$, B. $Pd(bqd)_2$, C. orthorhombic $Ni(bqd)_2$. From reference 36

Figure 9. Resonance Raman ($\nu_0 = 5145 \text{ \AA}$)(A) and iodine -129 Mössbauer (B) spectra of $\text{Ni(bqd)}_2\text{I}_{0.5}$ from reference 11.

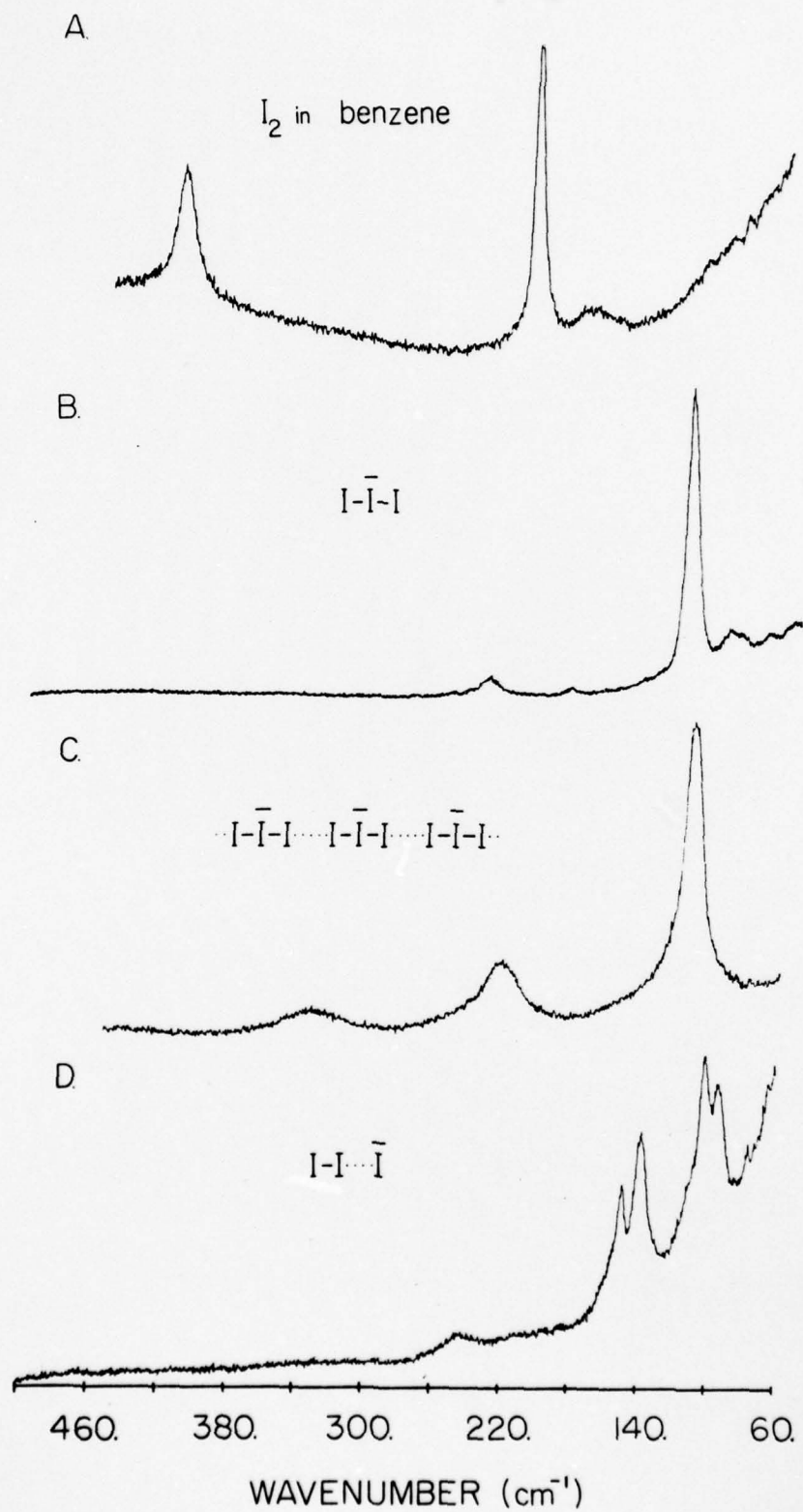
Figure 10. Resonance Raman spectra of partially oxidized metal phthalocyanine materials with 5145 \AA excitation.

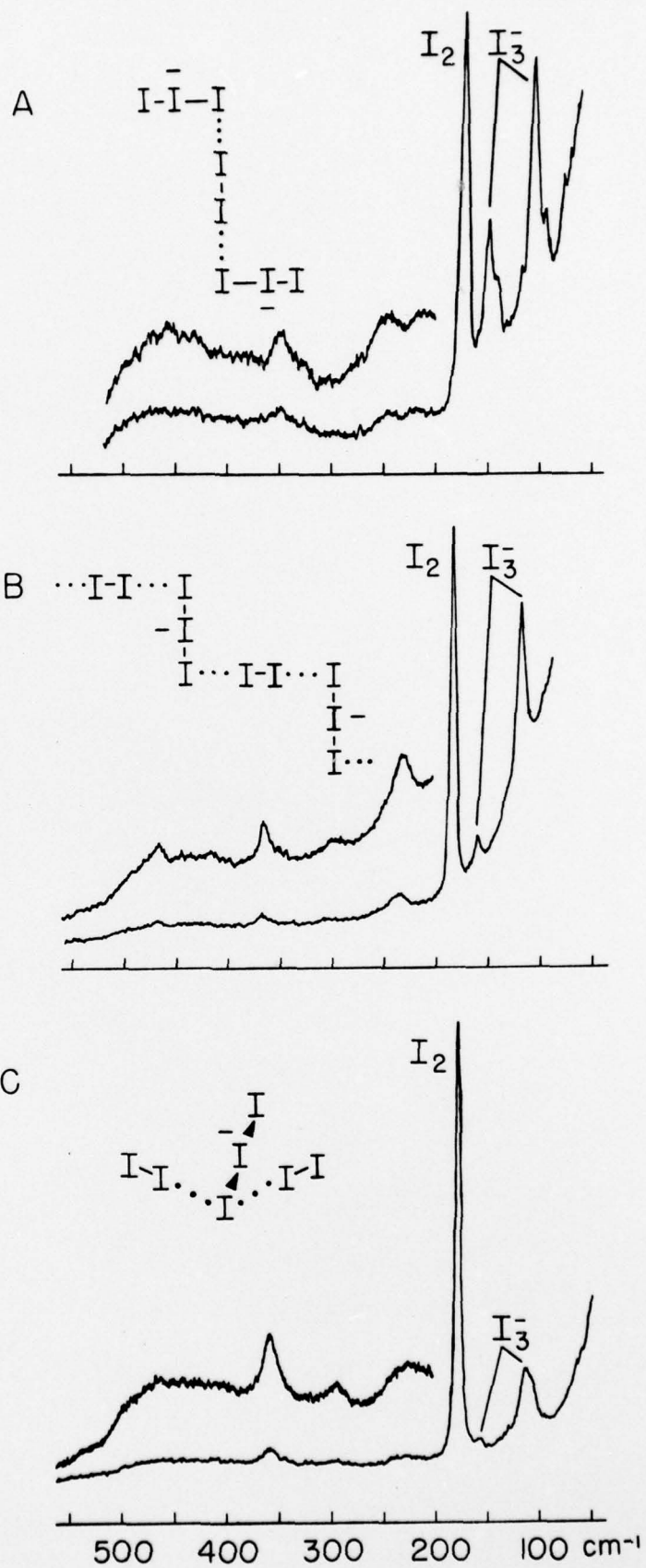
Figure 11. Iodine -129 Mössbauer spectrum of $\text{Ni(Pc)I}_{2.16}$ from reference 38.

Figure 12. View down the c axis of the unit cell of $\text{NiPcI}_{1.0}$ from reference 38.

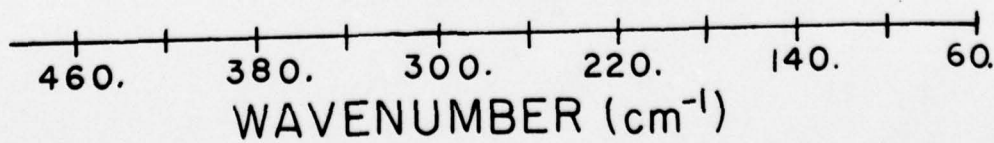
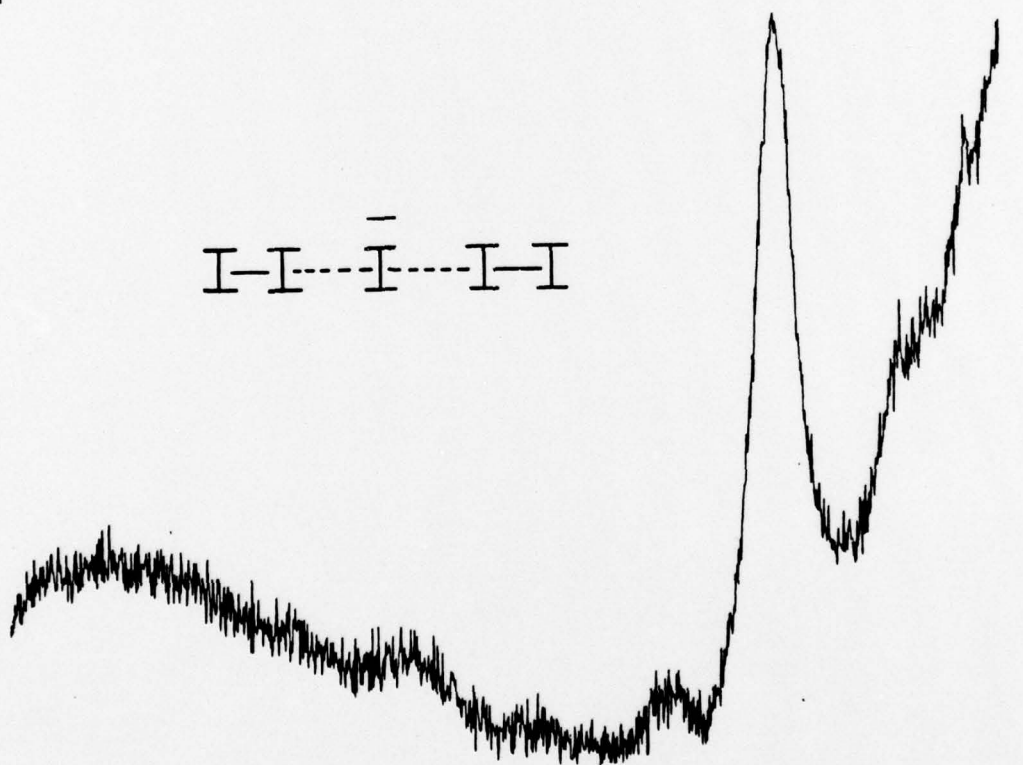
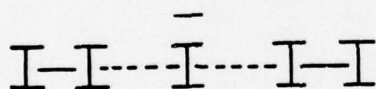
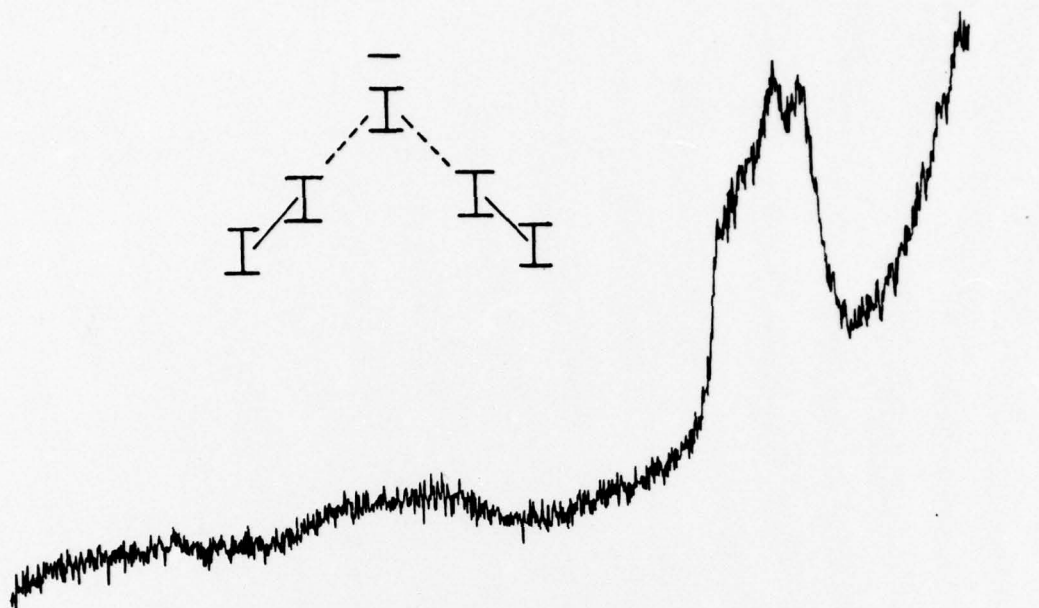
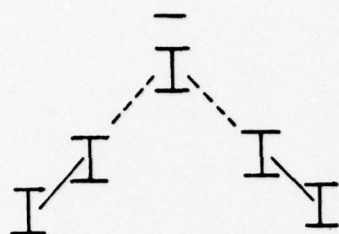
Figure 13. Electrical conductivity as a function of temperature for pressed pellet samples of various partially oxidized metal phthalocyanines, MPcI_x . Powder (—) and single crystal (----) data for (quinolinium)(TcNQ)₂ are also presented. From reference 37.

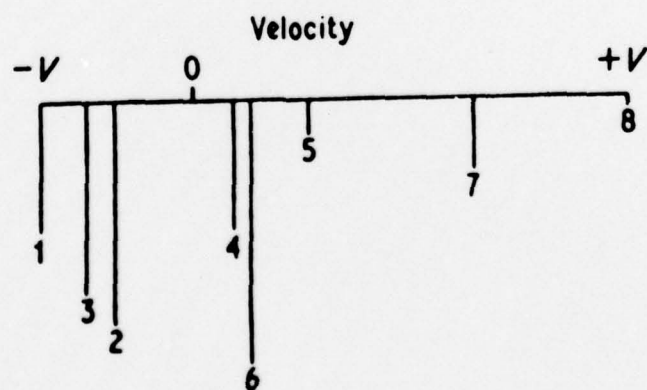
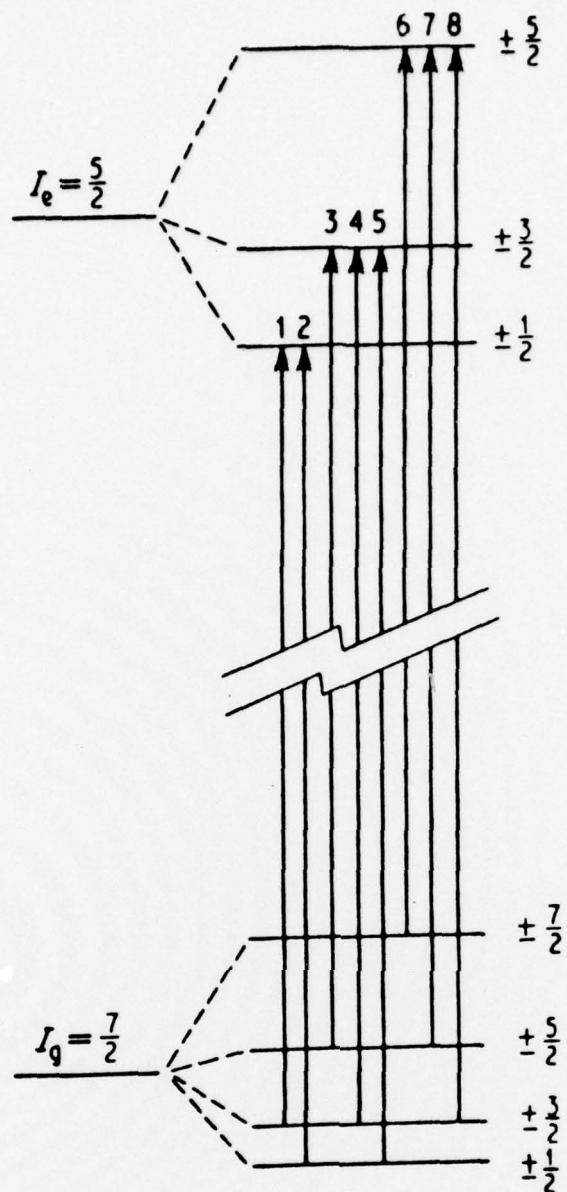
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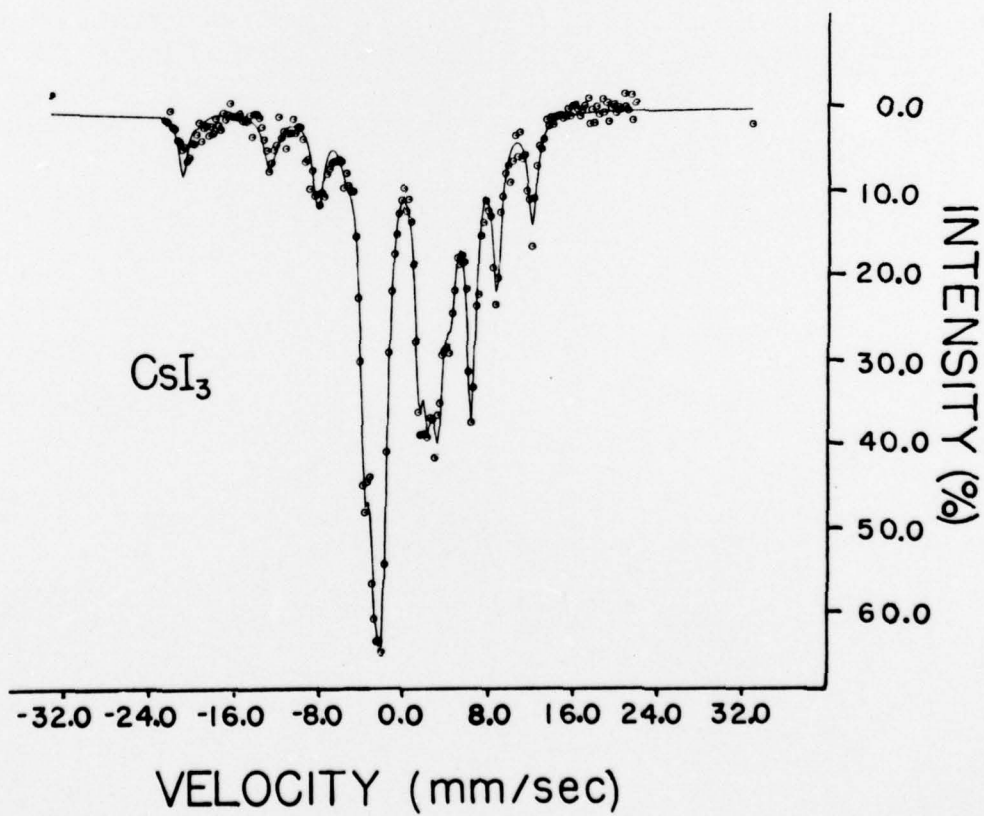
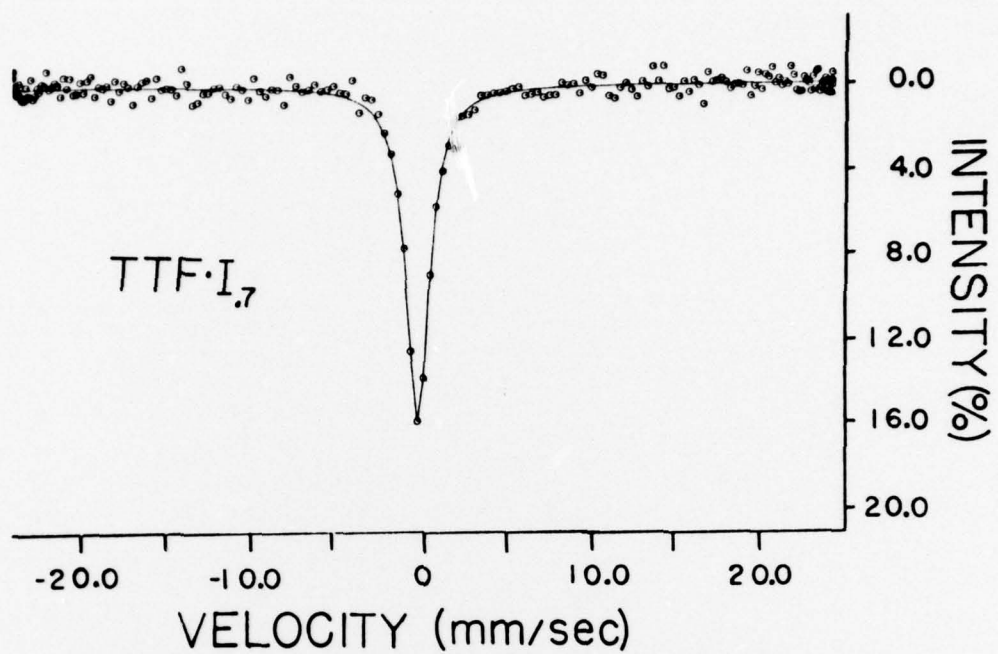


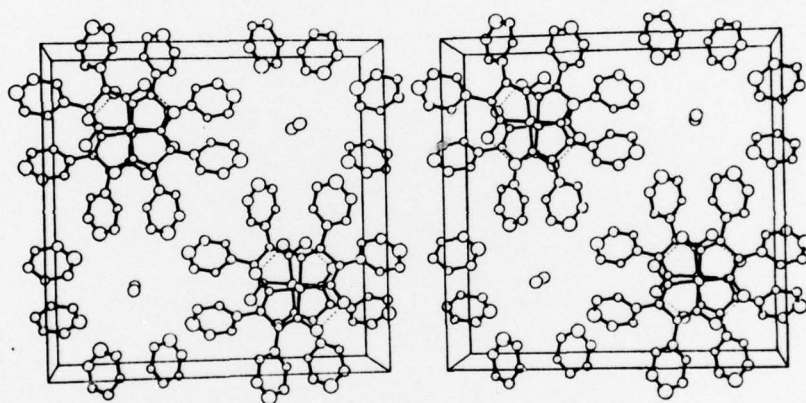
RESONANCE RAMAN

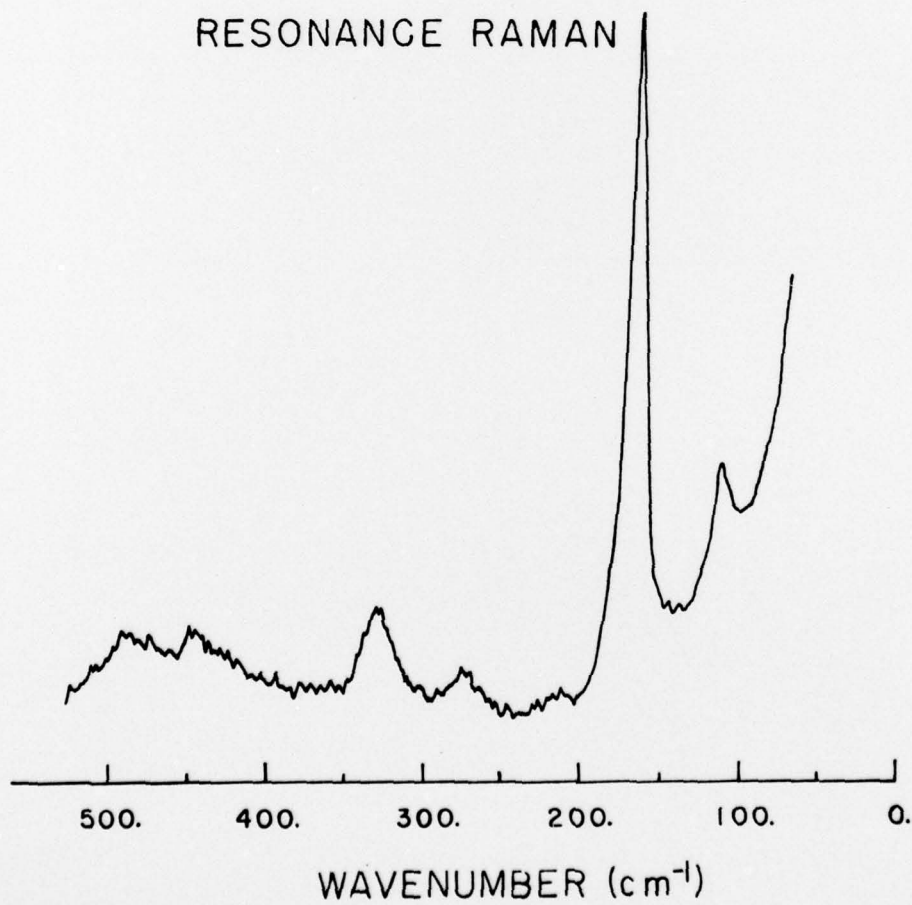
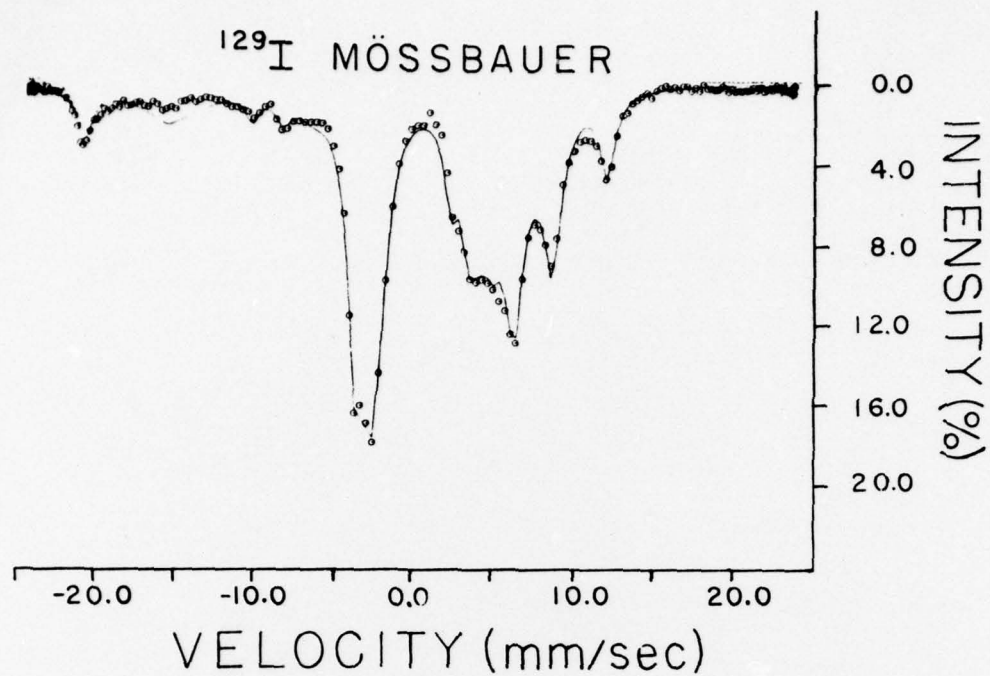
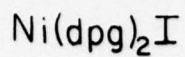


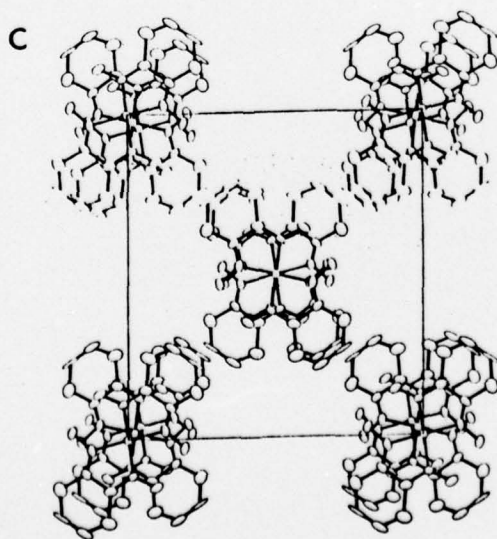
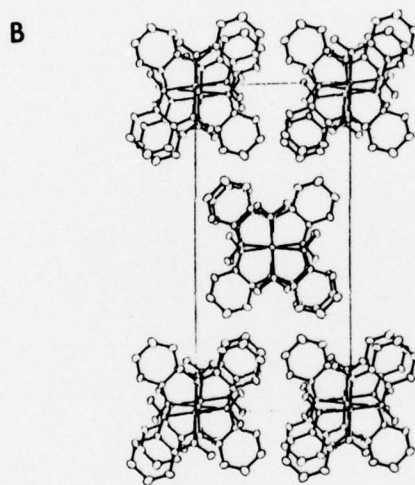
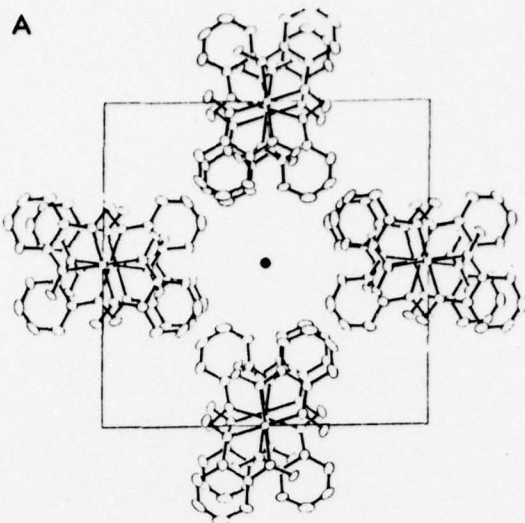


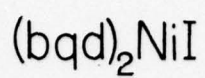
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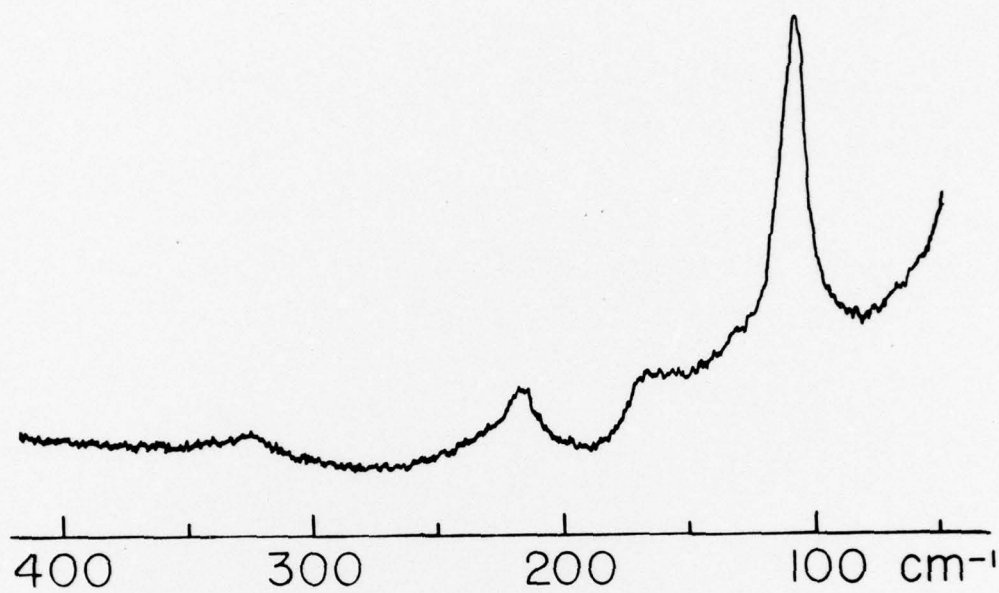




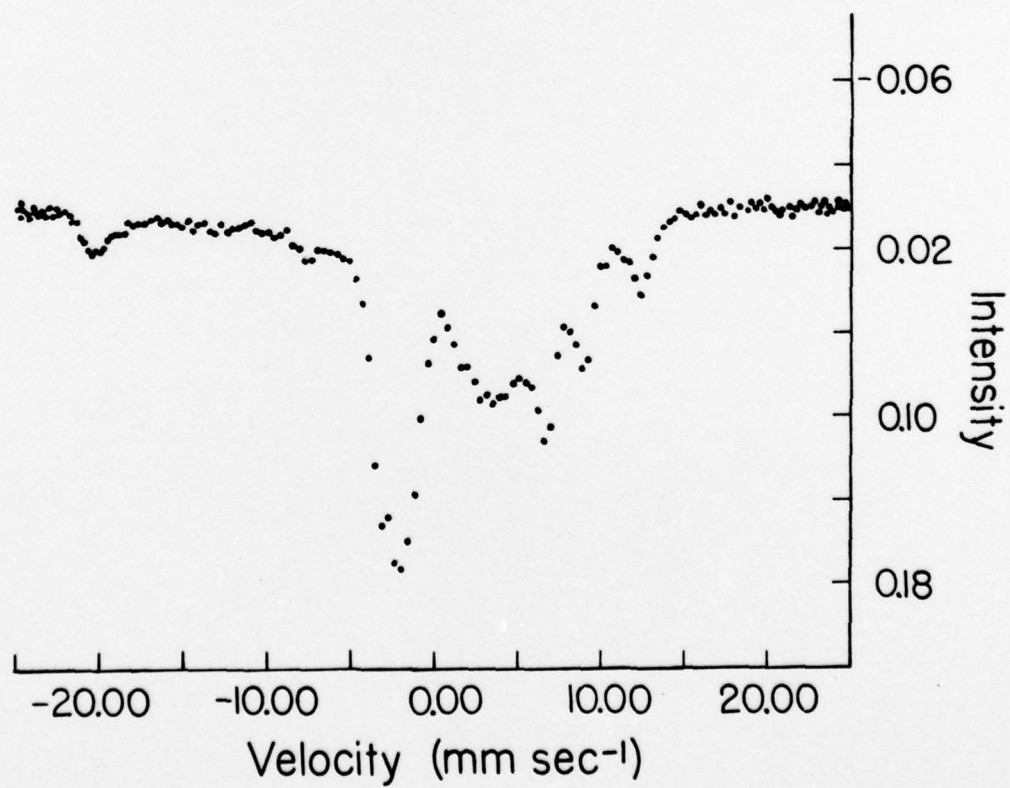


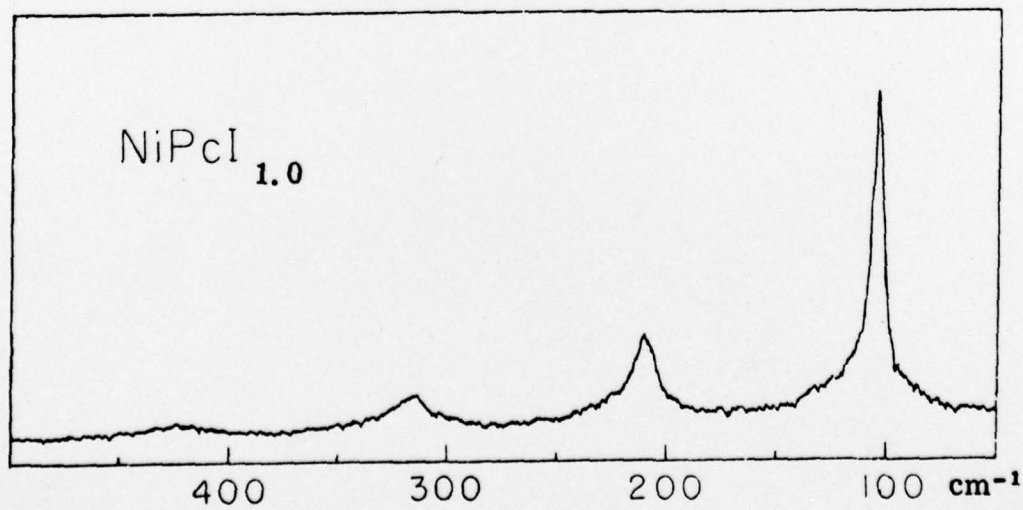
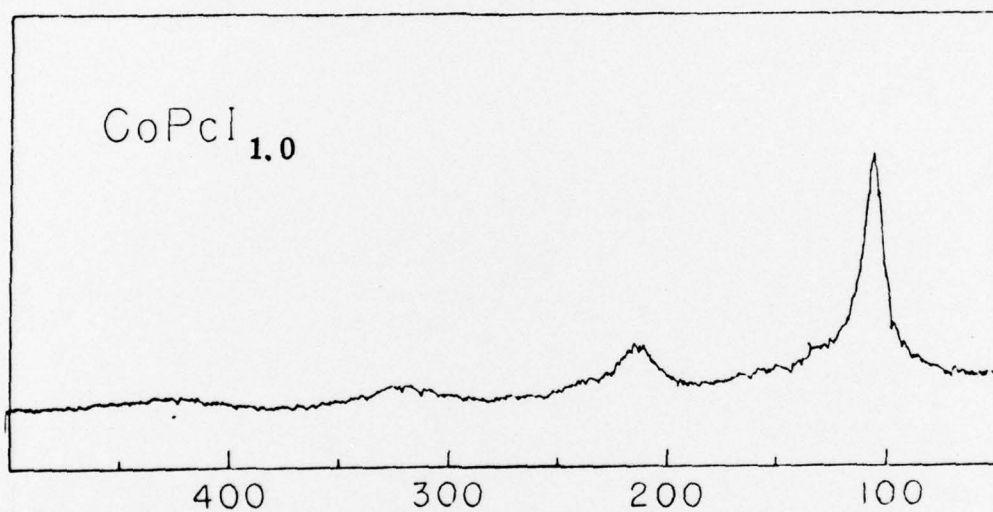
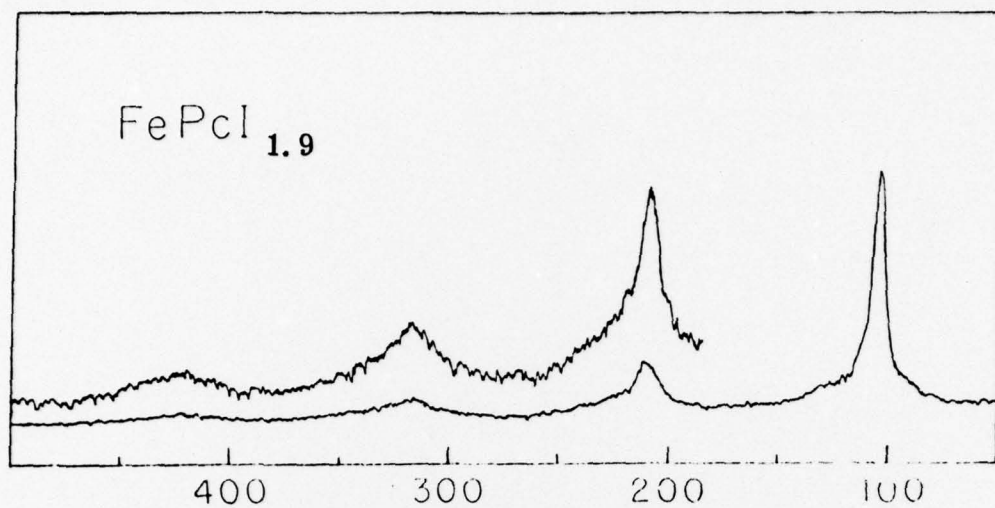


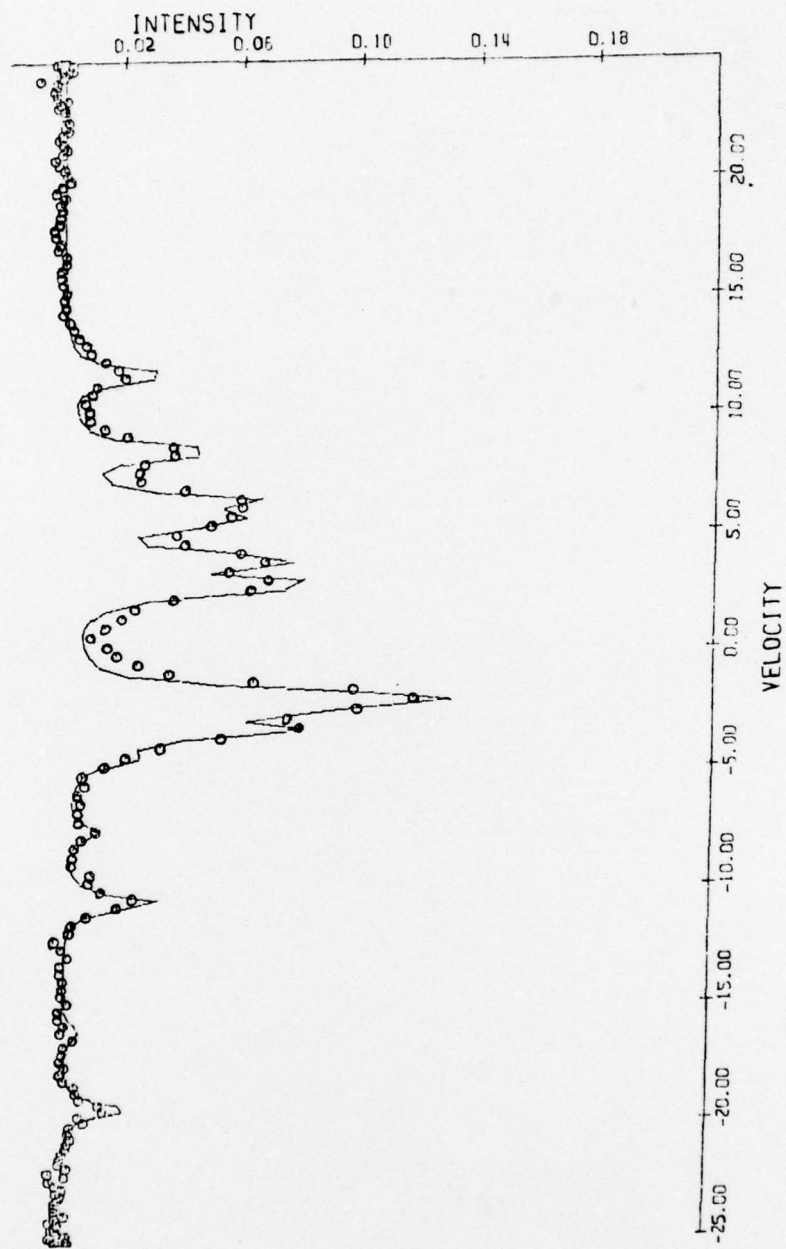
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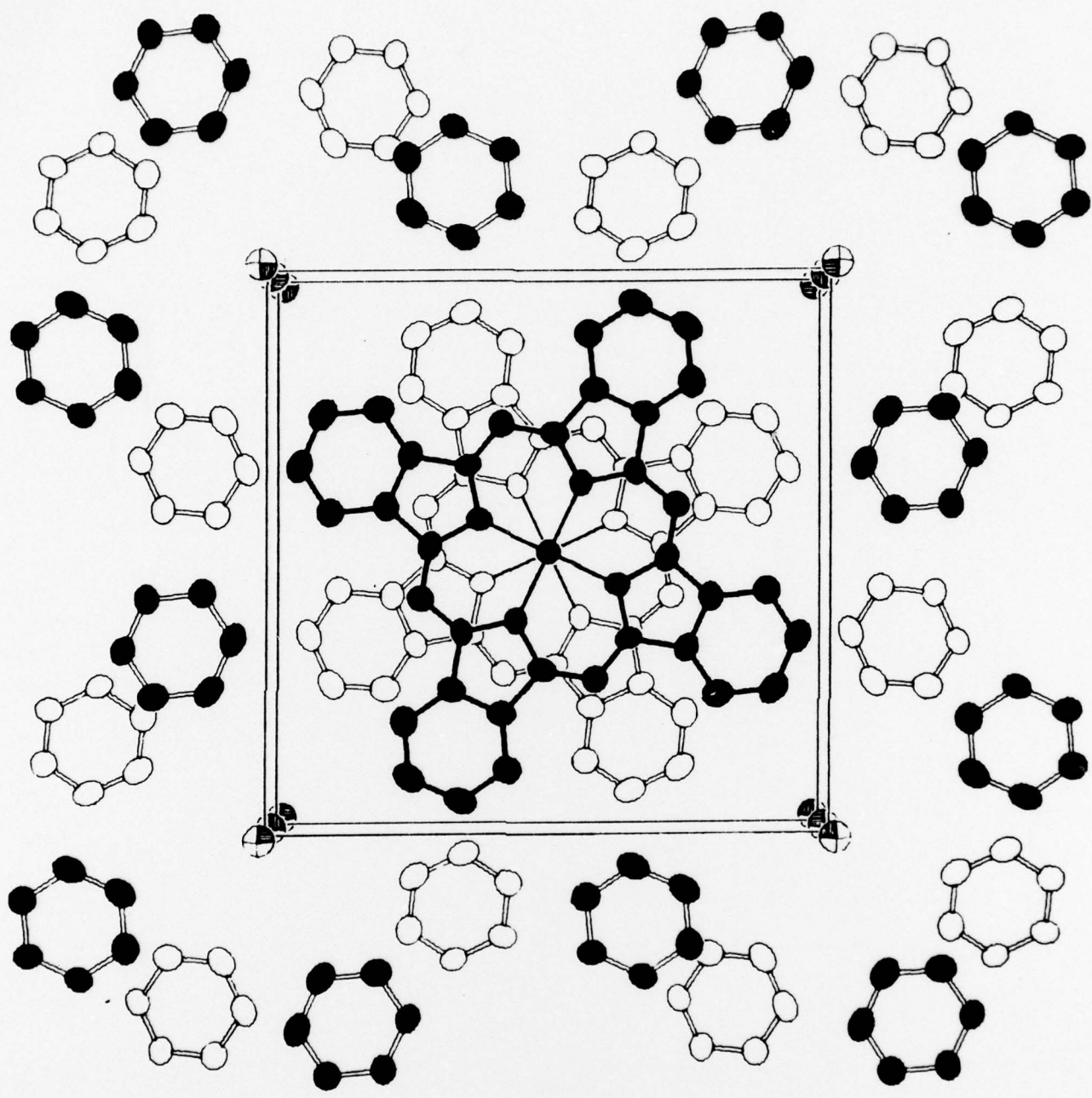


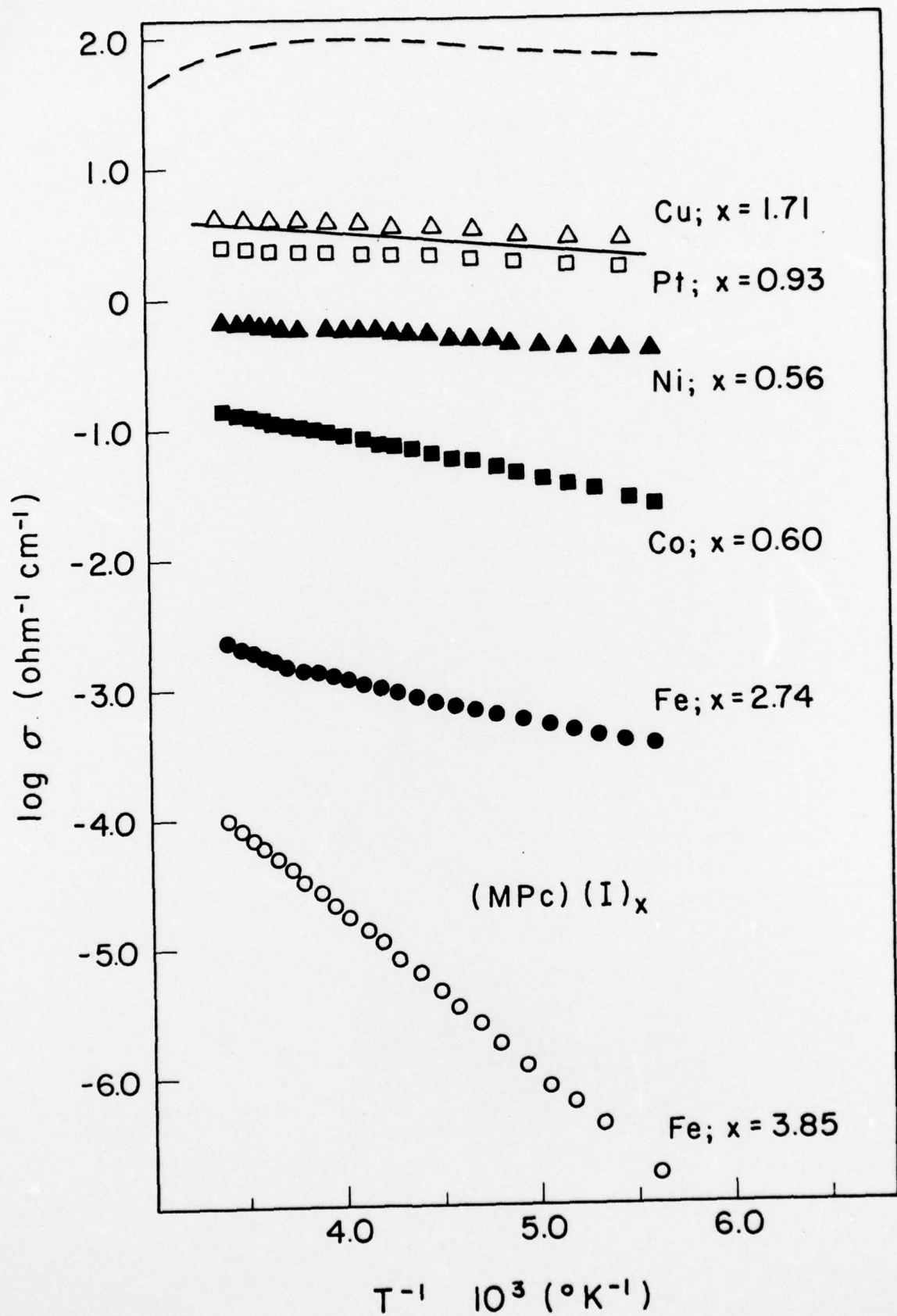
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